MATERIAL SAFETY DATA SHEET

1. SUBSTANCE AND SOURCE IDENTIFICATION

National Institute of Standards and Technology
Standard Reference Materials Program
SRM Number: 3122
MSDS Number: 3122

100 Bureau Drive, Stop 2320

Gaithersburg, Maryland 20899-2320

SRM Name: Hafnium Standard Solution

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Description: This Standard Reference Material (SRM) is intended for use as a primary calibration standard for the quantitative determination of hafnium. One unit of SRM 3122 consists of 50 mL of a single element solution in a high density polyethylene bottle sealed in an aluminized bag. The solution is prepared gravimetrically to contain a known mass fraction of Hafnium. The solution contains nitric and hydrofluoric acids at a volume fraction of approximately 10 % and 2 %, respectively.

Material Name: Hafnium Standard Solution

Other Designations:

Hafnium: Hf; elemental hafnium; celtium.

Hydrofluoric Acid: Hydrogen fluoride; fluorhydric acid.

Nitric Acid: Aqua fortis; hydronitrate; azotic acid; engraver's acid.

2. COMPOSITION AND INFORMATION ON HAZARDOUS INGREDIENTS

Component	CAS Registry	EC Number (EINECS)	Concentration (%)	
Nitric Acid	7697-37-2	231-714-2	10	
Hydrofluoric Acid	7664-39-3	231-634-8	2	
Hafnium	7440-58-6	231-166-4	1	

EC Classification, R/S Phrases: Refer to Section 15, Regulatory Information.

3. HAZARDS IDENTIFICATION

NFPA Ratings (Scale 0-4): Health = 4 Fire = 0 Reactivity = 2

Major Health Hazards: Nitric acid and hydrofluoric acid may cause death by inhalation, ingestion, or

absorption through the skin. Hafnium is primarily an irritant.

Physical Hazards: Container may rupture.

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Potential Health Effects

Inhalation: Either nitric acid or hydrofluoric acid, if inhaled, can damage the mucous

membranes and upper respiratory tract, causing spasm, inflammation of the larynx and bronchi, chemical pneumonitis, and pulmonary edema. Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. Teeth may also be damaged. Inhalation of hafnium dust (not present in this SRM) may irritate the respiratory tract; prolonged or repeated

exposure may cause pulmonary fibrosis.

Skin Contact: Nitric acid and hydrofluoric acid can cause severe skin burns. Effects may be

delayed. Hydrofluoric acid can also penetrate the skin and attack the underlying tissues and bone, causing profound hypocalcemia and death; chronic exposure can

damage bones and joints. Contact with hafnium may cause skin irritation.

Eye Contact: Nitric acid and hydrofluoric acid can cause severe eye irritation, corneal burns,

permanent eye damage, or blindness. Contact with hafnium may cause eye

irritation.

Ingestion: Nitric acid and hydrofluoric acid can cause severe burns and damage to the GI tract.

Ingestion of hafnium may irritate the GI tract, causing abdominal pain, nausea, vomiting, and diarrhea. Hafnium has caused liver damage in animals, but its toxicity has not been fully investigated. Many hafnium compounds are poisonous.

Nο

Medical Conditions Aggravated by Exposure: Pre-existing conditions affecting the eyes, skin, respiratory tract, GI tract, skeleton, liver, or other target organs or tissues.

Listed as a Carcinogen/ Potential Carcinogen:

	1 03	110
In the National Toxicology Program (NTP) Report on Carcinogens		<u>X</u>
In the International Agency for Research on Cancer (IARC) Monographs		<u>X</u>
By the Occupational Safety and Health Administration (OSHA)		X

4. FIRST AID MEASURES

Inhalation: Move the person to fresh air immediately. If not breathing, qualified personnel may start CPR or give oxygen if necessary. Get medical aid at once, and bring the container or label.

Skin Contact: Remove contaminated clothing and shoes. Flush affected skin with water for at least 15 minutes, then wash thoroughly with soap and water. If burns are severe or if skin irritation persists, get medical aid and bring the container or label. Wash contaminated clothing before reusing.

Eye Contact: Remove contact lenses (if any). Do not allow victim to rub eyes or keep eyes closed. Flush eyes with large amounts of running water for at least 30 minutes, keeping eyelids open and raising lids to remove all chemical. Get medical aid at once, and bring the container or label.

Ingestion: Contact a poison control center immediately for instructions. Wash out mouth with water, but do not induce vomiting. Get medical aid at once, and bring the container or label.

Note to Physician (Nitric Acid): Wash affected skin with 5% solution of sodium bicarbonate (NaHCO₂). Activated charcoal is of no value. <u>Do not give bicarbonate to neutralize the material.</u>

Note to Physician (Hydrofluoric Acid): Treat for chemical pneumonia. Monitor and correct for hypocalcemia, cardiac arrhythmias, hyperkalemia, and hypomagnesemia. Renal dialysis may be indicated. Test fluoride levels of exposed personnel.

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5. FIRE FIGHTING MEASURES

Fire and Explosion Hazards: Although nitric acid does not burn, it is a powerful oxidizing agent that can react with combustible materials to cause fires. Hydrofluoric acid may also ignite or explode on contact with combustible materials; it is a negligible fire hazard when exposed to heat or flames.

Extinguishing Media: Extinguishing Media: Use extinguishing media appropriate to the surrounding fire: water spray, dry chemical, carbon dioxide, or foam. Use a water spray to dilute nitric acid and hydrofluoric acid and to absorb liberated oxides of nitrogen. (These guidelines apply to the mixture; when the components are considered separately, different precautions may apply.)

Fire Fighting: Avoid inhalation of material or combustion byproducts. Wear full protective clothing and NIOSH-approved self-contained breathing apparatus (SCBA).

Flash Point (°C): N/A

Autoignition (°C): N/A for mixture Flammability Limits in Air: N/A Lower Explosive Limit (LEL): N/A Upper Explosive Limit (UEL): N/A Flammability Class (OSHA): N/A

6. ACCIDENTAL RELEASE MEASURES

Occupational Release: Notify safety personnel of spills. Surfaces contaminated with this material should be covered with soda ash or sodium bicarbonate to neutralize the acid. Place the neutralized material into containers suitable for eventual disposal, reclamation, or destruction.

Disposal: Refer to Section 13, Disposal Considerations.

7. HANDLING AND STORAGE

Storage: Store unopened containers of this material in a dry place at room temperature. Protect from physical damage, heat, and light, and isolate from incompatible materials. Use opened containers immediately or discard.

Safe Handling Precautions: Wear gloves and chemical safety goggles (Section 8). If contact with this material occurs, wash hands or change clothing as required. Engineering controls should maintain airborne concentrations below TLV (Section 8).

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

Nitric Acid:

ACGIH TLV-TWA: 2 ppm or 5 mg/m³

OSHA PEL: 2 ppm or 5 mg/m³

UK WEL: 5.2 mg/m³

Hydrofluoric Acid:

ACGIH TLV-TWA: 3 ppm or 2.5 mg/m³

OSHA PEL: 3 ppm or 2.5 mg/m³ UK WEL (8-hr TWA): 1.5 mg/m³

Hafnium:

ACGIH TLV-TWA: 5 mg/m³

OSHA PEL: 5 mg/m³

UK WEL (8-hr TWA): 0.5 mg/m³

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Ventilation: Use local or general exhaust to keep employee exposures below limits. Local exhaust ventilation is preferred because it can control contaminant emissions at the source, preventing dispersion into the general work area. Refer to the ACGIH document *Industrial Ventilation*, a Manual of Recommended Practices.

Respirator: If necessary, refer to the NIOSH document *Guide to the Selection and Use of Particulate Respirators Certified under 42 CFR 84* for selection and use of respirators certified by NIOSH.

Eye Protection: Use chemical safety goggles where dusting or splashing of solutions may occur. See OSHA standard (29 CFR 1910.133) or European Standard EN166. The employer should provide an emergency eye wash fountain and safety shower in the immediate work area.

Personal Protection: Wear appropriate gloves and protective clothing to prevent contact with skin.

9. PHYSICAL AND CHEMICAL PROPERTIES

Nitric Acid	Hydrofluoric Acid	Hafnium	
Appearance and Odor: Colorless to slightly yellow liquid darkens to brown upon aging and exposure to light; irritating, pungent odor.	Appearance and Odor: Colorless, fuming liquid; strong, irritating, pungent odor.	Appearance and Odor: Highly lustrous, ductile, grayish solid; no odor.	
Relative Molecular Weight: 63.02	Relative Molecular Weight: 20.01	Relative Molecular Weight: 178.5	
Molecular Formula: HNO ₃	Molecular Formula: HF	Molecular Formula: Hf	
Specific Gravity: 1.0543 (10%)	Specific Gravity: 1.1	Specific Gravity: 13.31	
Solvent Solubility: Decomposes in alcohol	Solvent Solubility: Soluble in alcohol, benzene, toluene, <i>m</i> -xylene, and tetralin.	Solvent Solubility: Soluble in hydrofluoric acid	
Water Solubility: Soluble	Water Solubility: Soluble	Water Solubility: Insoluble	
Boiling Point (°C): 86 (187°F)	Boiling Point (°C): 108 (226°F)	Boiling Point (°C): 4602 (8316°F)	
Vapor Pressure (Pa): 946 @20°C	Vapor Pressure (Pa): 3333 @20°C	Vapor Pressure (Pa): N/A	
Vapor Density (Air=1): 2.17	Vapor Density (Air=1): 1.97	Vapor Density (Air=1): N/A	
pH: 1.0 (0.1M solution)	pH: 1.0 (0.1M solution)	pH: N/A	

NOTE: The physical and chemical data provided are for the pure components. Physical and chemical data for this solution do not exist. The actual behavior of the solution may differ from the individual components.

10. STABILITY AND REACTIVITY			
Stability:	X_ Stab	leUnstable	
Stable at	normal tempe	eratures and pressure.	

Conditions to Avoid: Incompatible materials, heat, direct sunlight, moisture, mechanical damage.

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Incompatible Materials:

Nitric Acid: Incompatible with numerous materials including organic materials, plastics, rubber, chlorine, and metal ferrocyanide.

Hydrofluoric Acid: Incompatible with water (exothermic reaction and toxic fumes), metals (liberates hydrogen gas), silica (liberates silicon tetrafluoride). Other incompatibles: acetic anhydride, alkalis, ammonia, arsenic trioxide, calcium oxide, carbonates, concrete, cyanides, ethylenediamine, glass, leather, metal oxides, organic materials, phosphorus pentoxide, rubber, sodium hydroxide, sulfuric acid, vinyl acetate.

Hafnium: Incompatible with halogens and halocarbons (exothermic reaction), nitryl fluoride (incandescence), strong oxidizers, nitrogen, phosphorus, oxygen, sulfur, chlorates, nitrates, sulfates, molybdates, tungstate, borax, lead oxide, copper oxide.

Fire/Explosion Information: See Section 5.

Hazardous Decomposition: Thermal decomposition of this mixture may release halogenated (fluorinated) compounds and toxic or hazardous gases, including nitrogen oxides and hafnium oxides. Reactions with incompatible materials may release other hazardous products, such as hafnium halide vapors and flammable hydrogen gas.

Hazardous Polymerization: Will Occur		Occur X Will Not Occur			
11. TOXICOLOGICAL INFORMATION					
Route of Entry:	X Inhalation	X Skin	X Ingestion		
Nitric Acid:					

Human, oral: $LD_{Lo} = 430 \text{ mg/kg}$ Rat, oral: $LD_{50} > 90 \text{ mg/kg}$

Rat, inhalation: LC_{50} (4 hrs) = 130 mg/m³

Hydrofluoric Acid:

Human, oral: $TD_{Lo} = 143 \text{ mg/kg}$

Human, inhalation: TC_{Lo} (5 min.) = 100 mg/m³

Hafnium:

Mouse, oral: $LD_{50} = 76 \text{ mg/kg}$

Target Organ(s): Respiratory tract, skin, eyes, GI tract, teeth, skeleton, liver.

Mutagen/Teratogen: Nitric acid and hydrofluoric acid have caused birth defects and mutations in animals under experimental conditions. The toxicity of hafnium has not been fully investigated, but it is not classified as a reproductive hazard.

Health Effects: See Section 3.

12. ECOLOGICAL INFORMATION

Nitric Acid, Ecotoxicity Data:

Green shore crab (*Carcinus maenas*): LC_{50} (48 hrs) = 180,000 µg/L Starfish (*Asterias rubens*): LC_{50} (48 hrs) = 100,000 to 330,000 µg/L

Hooknose (Agonus cataphractus): LC_{50} (48 hrs) = 100,000 to 330,000 µg/L

Brook trout (*Salvelinus fontinalis*): NR-LETH = 1,562 μg/L

Cockle (*Cerastoderma edule*): LC_{50} (48 hrs) = 330,000 to 1,000,000 µg/L

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Hydrofluoric Acid: Acid soils can bind fluorides tightly. Plants may be damaged in soils with high calcium content, which can immobilize fluorides. Ecotoxicity data for HF:

Shrimp in aerated seawater: LC_{50} (48 hrs) = 300 ppm

Freshwater fish: lethal dose (endpoint and time period not specified) = 60 ppm

Hafnium: No ecotoxicity data found.

Environmental Summary: One or more components of this mixture may be toxic to aquatic organisms. Do not release to the environment.

13. DISPOSAL CONSIDERATIONS

Waste Disposal: One or more components of this mixture are a RCRA hazardous waste. Dispose of container and unused contents in accordance with federal, state, and local requirements for acid waste, which vary according to location. Decontaminate containers before recycling. Processing, use, or contamination of this product may change the waste management options.

14. TRANSPORTATION INFORMATION

U.S. DOT and IATA: Nitric Acid Solution: Hazard Class 8, UN2031, Packing Group II

15. REGULATORY INFORMATION

U.S. REGULATIONS

CERCLA Sections 102a/103 (40 CFR 302.4):

Nitric Acid: RQ = 1000 lbs. Hydrofluoric Acid: RQ = 1000 lbs.

Hafnium: Not regulated.

SARA Title III Section 302: Nitric acid and hydrofluoric acid are regulated.

SARA Title III Section 304: Nitric acid and hydrofluoric acid are regulated.

SARA Title III Section 313: Nitric acid and hydrofluoric acid are regulated.

OSHA Process Safety (29 CFR 1910.119): Nitric acid (> 94.5%) and hydrofluoric acid are regulated.

SARA Title III Sections 311/312 Hazardous Categories (40 CFR 370.21):

ACUTE: Yes CHRONIC: Yes FIRE: No REACTIVE: Yes SUDDEN RELEASE: No

STATE REGULATIONS

California Proposition 65: None of the components are regulated.

CANADIAN REGULATIONS

WHMIS Classification:

Nitric Acid: O (Oxidizing), C (Corrosive) Hydrofluoric Acid: T (Toxic), C (Corrosive)

Hafnium: D2B (toxic)

WHMIS Ingredient Disclosure List: All three components are regulated

CEPA Domestic Substances List (DSL): All three components are regulated

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EUROPEAN REGULATIONS

EU/EC Classification:

Nitric Acid: O (Oxidizing), C (Corrosive) Hydrofluoric Acid: T (Toxic), C (Corrosive)

Hafnium: Xn (Harmful); not classified in Annex I of Directive 67/548/EEC

Risk Phrases (mixture):

R23/24/25 (toxic by inhalation, in contact with skin, and if swallowed)

R35 (causes severe burns)

R36/37/38 (irritating to eyes, respiratory system and skin)

Safety Phrases (mixture):

S20/21 (when using, do not eat, drink or smoke)

S26 (in case of eye contact, rinse immediately and seek medical advice)

S28 (in case of skin contact, wash immediately)

S45 (in case of accident or illness, see doctor; show label)

S60 (dispose of this material and its container as hazardous waste)

NATIONAL INVENTORY STATUS

U.S. Inventory (TSCA): All three components are listed.

TSCA 12(b), Export Notification: None of the components are listed.

16. OTHER INFORMATION

Sources:

CRC Handbook of Chemistry and Physics, 53rd Edition. 1972-1973.

Hazardous Substances Data Bank (HSDB): Hafnium.

IUCLID Chemical Data Sheet: Hydrogen Fluoride. 19 February 2000.

IUCLID Chemical Data Sheet: Nitric Acid. 19 February 2000.

PAN Pesticide Database: Nitric Acid and Hydrofluoric Acid.

U.S. National Institute for Occupational Safety and Health, *NIOSH Pocket Guide to Chemical Hazards*, September 2005 edition. DHHS (NIOSH) Publication No. 2005-151.

U.S. National Institute of Standards and Technology, Certificate of Analysis: Standard Reference Material® 3122, Hafnium Standard Solution. 01 June 2004.

Disclaimer: Physical and chemical data contained in this MSDS are provided only for use as a guide in assessing the hazardous nature of the material. The MSDS was prepared carefully, using current references; however, NIST does not certify the data in the MSDS. The certified values for this material are given in the NIST Certificate of Analysis.

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